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(54) HIGH STRENGTH MARTENSITIC STAINLESS STEEL TUBE FOR OIL WELL AND ITS PRODUCTION METHOD

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a high strength martensitic stainless steel tube for an oil well having high strength of  $YS \geq 125$  ksi (860 MPa), excellent low temperature toughness and excellent CO<sub>2</sub> corrosion resistance and to provide its production method.

SOLUTION: This steel tube has a composition containing  $\leq 0.05\%$  C,  $\leq 0.50\%$  Si, 0.30 to 1.50% Mn,  $\leq 0.03\%$  P,  $\leq 0.005\%$  S, 11.0 to 17.0% Cr, 2.0 to 7.0% Ni,  $\leq 3.0\%$  Mo,  $\leq 0.05\%$  Al,  $\leq 0.20\%$  V,  $\leq 0.15\%$  N and  $\leq 0.005\%$  O and also satisfying  $Cr+Mo+0.3Si-40C-10N-Ni-0.3Mn \leq 10$  and has a tempered martensitic structure containing retained austenite by  $\leq 10\%$ .

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## DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention about the martensitic stainless steel tube for oil wells used for a crude oil or the oil well of natural gas, and a gas well, The oil well with very severe corrosive environment containing especially carbon dioxide (CO<sub>2</sub>), a chloride ion (Cl<sup>-</sup>), etc., It is related with the high strength martensitic stainless steel tube for oil wells which has the suitable outstanding corrosion resistance and low-temperature toughness to use it by a gas well, and more than yield strength:860MPa (125ksi).

[0002]

[Description of the Prior Art]In recent years, in consideration of the jump in an oil price, and drain-izing of the petroleum resources expected in the near future, development of a depths oil field which was not considered, the sour gas rice field where the corrosiveness by which 1 \*\* was abandoned has strong development, etc. prospers on a worldwide scale conventionally. Generally such an oil field and a gas field have very deep depth, and the atmosphere serves as severe corrosive environment which is an elevated temperature and contains CO<sub>2</sub> and Cl<sup>-</sup> etc. Therefore, the oil well pipe used for mining in such an oil field and a gas field is high intensity, and the construction material which moreover has corrosion resistance is required.

[0003]Under the environment containing CO<sub>2</sub> and Cl<sup>-</sup> etc., it is common that the martensite system stainless steel material excellent in CO-proof<sub>2</sub> corrosiveness which contains Cr 13% is used. It was required that the characteristics, such as corrosion resistance which was more excellent also in the martensite system stainless steel material of Cr, should have been provided 13% with aggravation of an operating environment. As opposed to such a demand, the martensitic stainless steel for oil well pipes which has improved corrosion resistance and

stress-corrosion-cracking-proof nature is proposed by JP,62-54063,A. In the martensitic stainless steel for oil well pipes indicated to JP,62-54063,A. In order to form super-low C in order to decrease carbide, and to prevent the segregation to the grain boundary of P and S, stress-corrosion-cracking-proof nature supposes that corrosion resistance will improve by performing addition of N and Mo again reduction of P and S, and by adding Ca further.

[0004]In JP,2-243740,A, one sort of Ti, Nb, V, and Zr or two sorts or more are contained, (Cr+Mo) : the martensite system stainless steel material for oil wells which adjusted to not less than 10.5%, and adjusted Cr, Mo, Si, and a Ni content so that it might become still more nearly single martensitic structure is proposed. In the martensite system stainless steel material for oil wells indicated to JP,2-243740,A, it is supposed that sulfide-proof stress-corrosion-cracking nature will improve by having composition which was described above. however, the intensity of the steel materials indicated to JP,62-54063,A and JP,2-243740,A -- at most -- it is below 110ksi (758MPa) in the yield strength YS.

[0005]The depth of an oil field and a gas field becomes deep, and the oil well pipe of the further high intensity is demanded. And these days, the oil-field development in a cold district is also becoming active, and is required to have the low-temperature toughness which was excellent in addition to high intensity in many cases. However, in the usual martensitic stainless steel, when intensity exceeded 95ksi, there was a problem of toughness falling extremely and stopping being equal to use. The intensity of the steel materials indicated to JP,62-54063,A and JP,2-243740,A is the intensity below 110ksi (758MPa) in the yield strength YS.

the steel materials indicated to JP,62-54063,A and JP,2-243740,A -- the yield strength YS -- the high intensity more than 125ksi (860MPa) -- and it is not expectable that it is alike and satisfied also in high toughness.

[0006]Therefore, by the oil well as which high intensity is required, and the gas well, expensive 2 phase stainless steel which performed cold work had to be used conventionally. Since it was such, it has CO-proof<sub>2</sub> corrosiveness which was excellent in the cheap 13%Cr system as an object for oil well pipes, and development of the high strength martensitic stainless steel tube which was moreover excellent in low-temperature toughness was desired strongly.

[0007]

[Problem(s) to be Solved by the Invention]This invention is a martensitic stainless steel tube which contains Cr 13% in view of the problem of the above-mentioned conventional technology. The purpose shows corrosion resistance, such as CO-proof<sub>2</sub> corrosiveness outstanding under the severe corrosive environment containing CO<sub>2</sub> and Cl<sup>-</sup> etc., And it is providing a high strength martensitic stainless steel tube for oil wells which has the high

intensity more than 125ksi (860MPa), and the outstanding low-temperature toughness with the yield strength YS, and a manufacturing method for the same.

[0008]

[Means for Solving the Problem] Its attention is paid to a 13%Cr martensitic stainless steel tube first considered to be suitable for an oil well pipe in respect of CO-proof<sub>2</sub> corrosiveness in order that this invention persons may attain the above-mentioned technical problem, High intensity of 860 or more MPa and outstanding low-temperature toughness were wholeheartedly studied about a policy for making it provide with corrosion resistance with the yield strength YS to this martensitic stainless steel tube.

[0009] As a result, while this invention persons' reducing C in Cr steel more remarkably than before 13%, and carrying out increase-in-quantity content of nickel, Mo, and the V and reducing S, Si, aluminum, and O further, While good hot-working nature and corrosion resistance were secured by adjusting content of Cr, Mo, Si, C, N, nickel, and Mn so that a fixed expression of relations may be satisfied, it found out that low-temperature toughness which is the high intensity of 860 or more MPa in YS, and was excellent was acquired.

[0010] This invention is completed based on the above-mentioned knowledge. The 1st this invention is mass% and Namely, C:0.05% or less and less than Si:0.50%. Mn : 0.30 to 1.50%, P:0.03% or less, and below S:0.005 %. Cr : 11.0 to 17.0%, nickel:2.0 - 7.0 %, and below Mo:3.0 %. aluminum: Below O:0.005 % is included 0.05% or less, V:0.20% or less, and N:0.15% or less, and it is following (1) type Cr+Mo+0.3Si-40C-10 N-nickel-0.3Mn  $\leq 10$ ..... (1) (Cr, Mo, Si, C, N, nickel, and content (mass%)) of Mn:each element being satisfied here, and with a presentation which consists of the remainder Fe and inevitable impurities. Corrosion resistance having an organization which contains retained austenite 10% or less by an area rate, Are a high strength martensitic stainless steel tube for oil wells which is excellent in low-temperature toughness and has more than yield strength:860MPa, and in the 1st this invention. In addition to said presentation, at mass%, it is still more preferred to contain less than Nb:0.20%, and in the 1st this invention. In addition to said each presentation, at mass%, it is still more preferred to contain below Cu:3.5 %, and in the 1st this invention. In addition to said each presentation, at mass%, it is still more preferred to contain Ca:0.0005-0.01%, and in the 1st this invention. It is preferred that below Ti:0.3 % and below Zr:0.2 % contain two of one sort or the sorts or more below W:3.0 % B:0.01% or less at mass% further in addition to said each presentation.

[0011] The 2nd this invention is mass% and C:0.05% or less and less than Si:0.50%. Mn : 0.30 to 1.50%, P:0.03% or less, and below S:0.005 %. Cr : 11.0 to 17.0%, nickel:2.0-7.0 %, and below Mo:3.0 %. aluminum: It is following (1) type Cr+Mo+0.3Si-40C-10 N-nickel-0.3Mn  $\leq 10$  in 0.05% or less, V:0.20% or less, N:0.15% or less, and below O:0.005 %..... (1)

(steel stock which has the presentation included so that Cr, Mo, Si, C, N, nickel, and content (mass%)) of Mn:each element may be satisfied here, It is tempering temperature to a this steel pipe after considering it as a steel pipe by hot working. Corrosion resistance performing temper processing made into 500 - 590 \*\*, Yield strength which is excellent in low-temperature toughness: It is a manufacturing method of a high strength martensitic stainless steel tube for 860 or more MPa class oil wells, and quenching treatment cooled after heating to 890 - 950 \*\* before said temper processing may be performed in the 2nd this invention.

[0012]

[Embodiment of the Invention]The high strength martensitic stainless steel tube of this invention is a steel pipe which the yield strength YS has the high intensity of 125 or more (860 or more MPa) ksi, and was excellent in low temperature toughness. First, the reason for presentation limitation of this invention steel pipe is explained. It is only hereafter described as % mass%.

By this invention, although it is an element required in order that C:0.05%or less C may secure the intensity of a martensitic stainless steel tube, since nickel is contained, it will anneal, if contained so much and sensitization sometimes happens easily. For this reason, in this invention, C could be 0.05% or less. Although it is preferred to reduce C as much as possible from a corrosion-resistant viewpoint, it is preferred that C considers it as 0.001 to 0.03% of range in consideration of strong reservation.

[0013]Si: Although 0.50%or less Si is an element required as a deoxidizer in the usual steel-manufacture process, if it exceeds 0.50%, it will reduce CO-proof<sub>2</sub> corrosiveness and will also reduce hot-working nature further. For this reason, Si was limited to 0.50% or less.

Mn: Although it is an element required in order that Mn may secure the intensity of a martensitic stainless steel tube 0.30 to 1.50% and 0.30% or more of content is needed in this invention, if contained exceeding 1.50%, it will have an adverse effect on toughness. For this reason, Mn was limited to 0.30 to 1.50% of range.

[0014]Although both P:0.03%or less P is elements which degrade CO-proof<sub>2</sub> corrosiveness, CO-proof<sub>2</sub> stress-corrosion-cracking nature, pitting-proof nature, and sulfide-proof stress-corrosion-cracking nature and decreasing as much as possible is desirable, extreme reduction causes the rise of a manufacturing cost. For this reason, P was industrial comparatively cheaply feasible, and could be 0.03% or less which is a range which does not degrade CO-proof<sub>2</sub> corrosiveness, CO-proof<sub>2</sub> stress-corrosion-cracking nature, pitting-proof nature, and sulfide-proof stress-corrosion-cracking nature.

[0015]S: Although below 0.005 % S is an element which degrades hot-working nature remarkably and it is desirable to decrease as much as possible also for the productivity drive in a steel pipe manufacturing process, extreme reduction causes the rise of a manufacturing

cost. 0.005 When decreasing below to %, since steel pipe manufacture at the usual process was attained, the maximum of S was made into 0.005 %. It is below 0.003 % preferably.

[0016]Cr: 11.0 to 17.0%, in order that Cr may hold CO-proof<sub>2</sub> corrosiveness and CO-proof<sub>2</sub> stress-corrosion-cracking nature, it is main elements and not less than 11.0% of content is needed from a corrosion-resistant viewpoint, but if contained exceeding 17.0%, hot-working nature will deteriorate. From this, Cr was limited to 11.0 to 17.0% of range.

[0017]nickel: 2.0 - 7.0 %nickel is an element which has the operation which strengthens a protective film and improves CO-proof<sub>2</sub> corrosiveness, CO-proof<sub>2</sub> stress-corrosion-cracking nature, pitting-proof nature, and sulfide-proof stress-corrosion-cracking nature by that cause, and is also an element to which the intensity of a steel pipe is made to increase by solid solution strengthening. By this invention which reduces C, although nickel is added by the key objective in the increase in intensity, by content of less than 2.0 %, the content in which the effect is not accepted but exceeds 7.0 % on the other hand spoils the stability of martensitic structure. From this, nickel was limited to the range of 2.0 - 7.0 %.

[0018]Below Mo:3.0 %Mo is an element to which the resistance over pitting by Cl<sup>-</sup> is made to increase, 0.5 Although it is desirable that more than % contains, if contained exceeding 3.0 %, generating of a delta ferrite will be caused and CO-proof<sub>2</sub> corrosiveness, CO-proof<sub>2</sub> stress-corrosion-cracking nature, and hot-working nature will be reduced. The content which Mo is an expensive element and exceeds 3.0 % becomes disadvantageous economically. Since it was such, Mo was limited to below 3.0 %. It is below 1.5 % preferably.

[0019]aluminum: Although 0.05% or less aluminum is an element which has powerful deacidification, the content exceeding 0.05% has an adverse effect on toughness. For this reason, aluminum was limited to 0.05% or less. It is 0.02 to 0.04% preferably.

V: Although it is an element which has the operation which 0.20% or less V makes intensity increase, and improves stress-corrosion-cracking-proof nature, the content exceeding 0.20% degrades toughness. For this reason, V was limited to 0.20% or less. It is 0.03 to 0.10% preferably.

[0020]Although it is desirable to be an element raised remarkably and to contain pitting-proof nature 0.01% or more as for N:0.15% or less N, the content exceeding 0.15% forms various nitrides, and degrades toughness. For this reason, N was limited to 0.15% or less of range.

O: In order for below 0.005 % O to demonstrate the performance of this invention steel pipe enough, it is a very important element and decreasing as much as possible is preferred. That is, if there is much O content, various kinds of oxides will be formed and hot-working nature, CO-proof<sub>2</sub> stress-corrosion-cracking nature, pitting-proof nature, sulfide-proof stress-corrosion-cracking nature, and toughness will be reduced remarkably. For this reason, O was limited to below 0.005 %.

[0021]the presentation above-mentioned in this invention -- in addition -- further -- Nb, Ca, or Cu -- it can be independent, or it compounds and can contain. In addition to the above-mentioned presentation, one sort of Ti, Zr, B, and W or two sorts or more can be chosen and contained. the above-mentioned presentation -- in addition, Nb, Ca, or Cu -- it compounds and contains, and it can be independent, or one sort of Ti, Zr, B, and W or two sorts or more are chosen further, and it can contain.

[0022]Nb: Although it is an element which has the operation which Nb forms [ operation ] carbide, raises intensity 0.20% or less, and improves toughness, the content exceeding 0.20% reduces toughness conversely. For this reason, as for Nb, limiting to 0.20% or less is preferred.

Ca: 0.0005 to 0.01%Ca is an element which fixes S as CaS, spheroidizes inclusion S system, makes the lattice strain of the matrix around inclusion small, lowers the trap ability of hydrogen, and raises waterproof matter crack nature. Although such an effect becomes remarkable by 0.0005% or more of content, it exceeds 0.01%, and content causes the increase in CaO and reduces CO-proof<sub>2</sub> corrosiveness and pitting-proof nature. For this reason, as for Ca, limiting to 0.0005 to 0.01% is preferred. It is 0.001-0.005 % more preferably.

[0023]Below Cu:3.5 % Cu strengthens a protective film, and it controls invasion of hydrogen to the inside of a steel pipe, It is an element which improves sulfide-proof stress-corrosion-cracking nature, when adding, it is desirable that more than 0.3 % contains, but if contained exceeding 3.5 %, CuS will carry out a grain boundary deposit at an elevated temperature, and hot-working nature will fall. As for this to Cu, limiting to below 3.5 % is preferred.

[0024]Ti: B:0.01% or less, each of one sort or two or more sort Ti below W:3.0 %, Zr, B, and W raises intensity, and has the operation which improves stress-corrosion-cracking-proof nature, and below 0.3 % and below Zr:0.2 % can choose and contain it by this invention if needed. As for Ti, if Zr exceeds 0.3 %, B exceeds 0.2 %, and W exceeds 3.0 % 0.01%, respectively, and contained, in order to degrade toughness, it is [ Ti ] preferred that B considers it as 0.01% by 0.3 % and Zr considering it as 0.2 %, and W makes 3.0 % a maximum, respectively. At less than 0.0005%, since B has few above-mentioned effects, it is more preferred to consider it as 0.0005% or more. That is, as for Ti, it is preferred that below 0.3 % limits Zr to below 0.2 %, and W limits B to below 3.0 % 0.01% or less.

[0025]The remainders other than the above-mentioned ingredient are Fe and inevitable impurities. It is in the composition range which described above the content of Cr, Mo, Si, C, N, nickel, and Mn further in this invention, and is following (1) type Cr+Mo+0.3Si-40C-10 N-nickel-0.3Mn<=10..... (1)

It adjusts so that Cr, Mo, Si, C, N, nickel, and the content (mass%) of Mn:each element may be satisfied here. (1) A value of the formula left side = if Cr+Mo+0.3Si-40C-10 N-nickel-0.3Mn exceeds ten, even if desired intensity is satisfied, low temperature toughness will deteriorate.

For this reason, in this invention, A value was limited to ten or less.

[0026]this invention steel pipe has the tempering martensitic structure which contains retained austenite 10% or less by an area rate. If the amount of retained austenites exceeds 10% by an area rate, it will become difficult for it to be stabilized and to secure high intensity. Below, the manufacturing method of this invention steel pipe is explained. Let steel stock of the above-mentioned presentation be a steel pipe by hot working. It is not necessary to limit in particular for the manufacturing method of steel stock in this invention. After ingoting the molten steel of the presentation above-mentioned by the usually publicly known ingot methods, such as a converter and an electric furnace, or adding secondary [ further ] refinement etc., it is preferred to consider it as steel stock with usually publicly known casting methods, such as a continuous casting process.

[0027]It is not necessary to limit in particular for the hot working method of steel stock, and what is necessary is just to consider it as seamless steel tubes in this invention using the manufacturing process of the usual seamless steel tubes. As a manufacturing process of seamless steel tubes, the manufacturing process by hot working, such as a mandrel mill method and a plug mill method, is a desirable manufacturing process. It is good also as a steel pipe using the manufacturing process of electroseamed steel pipes other than seamless steel tubes, and a UOE steel pipe.

[0028]Tempering temperature after hardening treatment which heats the steel pipe manufactured by hot working to the temperature requirement of 890 - 950 \*\* with hot working, and is cooled was performed Temper processing made into 500 - 590 \*\* is performed. If tempering temperature exceeds 590 \*\* in less than 500 \*\*, it cannot be stabilized, austenite cannot be deposited 10% or less by an area rate, and high intensity and the outstanding low temperature toughness cannot be provided. The amount of austenites which deposits if austenite does not deposit and tempering temperature exceeds 590 \*\* by less than 500 \*\* increases too much, and intensity falls. in addition -- it is not necessary to limit cooling in particular in tempering treatment -- air cooling or water cooling -- any may be sufficient.

[0029]Cooking temperature becomes in the hardening treatment before tempering treatment, equalization of an organization may become insufficient by less than 890 \*\*, if 950 \*\* is exceeded, big and rough-ization of a crystal grain may arise, and it may become a cause of toughness degradation. For this reason, as for the cooking temperature of hardening treatment, it is preferred to consider it as the temperature requirement of 890 - 950 \*\*. in addition -- it is not necessary to limit cooling in particular in hardening treatment -- air cooling or water cooling -- any may be sufficient.

[0030]

[Example]100 after fully carrying out degasifying of the molten steel of the presentation shown in Table 1 It was considered as the kilo steel ingot and the pipe (steel pipe) of the outer



diameter 3.3 inch (83.8mmphi) and the thickness 0.5 inch (12.7 mm) was produced with the model seamless rolling mill for research. Subsequently, each piece raw material of a pipe blank test was cut down, air cooling was carried out after 1-hour heating by 920 \*\*, and annealing for 30 minutes was given by further 540 - 620 \*\*.

[0031]About the obtained pipe, an organization, tractive characteristics, low-temperature toughness, and corrosion resistance were investigated.

(1) Organization each piece of a pipe blank test was extracted, and the organization was observed in the section (C section) which intersects perpendicularly with the direction of a tube length hand using the scanning electron microscope. Using X-ray diffractometer, the amount of retained austenites (gamma) under organization extracted the piece of the direction section blank test of C of the pipe (10mm thickness x10mmx10mm), and computed it from the ratio of the diffraction intensity from (220) of gamma, and the diffraction intensity from (211) of alpha.

(2) From tractive-characteristics each pipe, the JIS No. 10 specimen was extracted from the longitudinal direction of the steel pipe, the tensile test was carried out, and yield strength YS and tensile strength TS were calculated.

(3) Low-temperature-toughness low temperature toughness carried out and evaluated the Charpy impact test. The JIS No. 4 specimen was extracted from each pipe, the Charpy impact test was carried out at test temperature:-20 \*\*, and absorbed energy  $\sqrt{E_{-20}}$  was calculated.

(4) From corrosion-resistant each pipe, the corrosion spool with a 3 mm[ in thickness ] x30-mm x length of 40 mm was extracted by machining, the corrosion test was carried out in the autoclave, and corrosion resistance was evaluated. [ in width ] The conditions of the corrosion test were made into the conditions immersed for two weeks in the 20 mass % NaCl aqueous solution of CO<sub>2</sub> gas:30 atmosphere and temperature:150 \*\*. The weight of the specimen was measured after the corrosion test and corrosion weight loss was calculated. The existence of pitting was observed for the test piece surface after a corrosion test with 10 times as many magnifying glasses.

[0032]The existence of pitting generating of the corrosion rate calculated from this corrosion weight loss and a test piece surface estimated corrosion resistance. These results are shown in Table 2.

[0033]

[Table 1]

鋼素 材 No.	化 学 組 成 (mass%)													焼戻し 温度 (℃)
	C	Si	Mn	P	S	Al	Cr	Ni	Mo	V	N	O	その他	
A	0.026	0.19	0.51	0.02	0.001	0.01	13.4	4.34	0.44	0.051	0.076	0.0024	—	7.60
B	0.024	0.28	0.43	0.01	0.001	0.02	12.7	3.54	1.10	0.034	0.025	0.0048	Nb:0.035	9.01
C	0.027	0.23	0.45	0.01	0.001	0.01	13.4	3.68	1.29	0.052	0.037	0.0045	Ti:0.047	9.49
D	0.010	0.31	0.42	0.02	0.001	0.01	12.7	5.13	2.49	0.041	0.062	0.0037	Zr:0.016	9.01
E	0.021	0.20	0.45	0.02	0.001	0.02	13.1	5.06	0.88	0.038	0.038	0.0043	—	7.63
F	0.017	0.22	0.44	0.02	0.001	0.01	13.4	3.75	0.93	0.042	0.063	0.0028	Ti:0.031, W:0.520	9.20
G	0.025	0.24	0.61	0.02	0.001	0.01	13.4	4.09	0.16	0.085	0.035	0.0039	Ca:0.002	8.01
H	0.023	0.25	0.33	0.01	0.002	0.02	12.9	4.19	0.26	0.065	0.056	0.0048	Ti:0.022, B:0.001	7.47
I	0.022	0.30	0.62	0.02	0.001	0.02	13.8	3.68	0.91	0.037	0.028	0.0032	Zr:0.012	9.77
J	0.011	0.24	0.49	0.02	0.001	0.02	13.6	5.51	0.64	0.051	0.046	0.0029	Cu:0.340	7.76
K	0.023	0.24	0.39	0.02	0.002	0.02	13.1	0.76	0.75	0.010	0.061	0.0013	—	11.52
L	0.026	0.26	0.41	0.01	0.001	0.02	10.4	3.09	0.45	0.047	0.037	0.0035	—	6.31
M	0.059	0.31	0.46	0.02	0.001	0.01	12.6	3.55	0.77	0.031	0.018	0.0026	Ti:0.025	7.24
N	0.027	0.21	0.46	0.02	0.001	0.02	13.5	1.53	0.47	0.018	0.026	0.0036	—	11.03
O	0.026	0.34	0.44	0.02	0.001	0.02	13.4	4.97	0.18	0.046	0.012	0.0039	—	7.42
P	0.028	0.21	0.43	0.01	0.001	0.01	13.0	2.15	1.45	0.055	0.078	0.0018	Ti:0.014	10.33
Q	0.017	0.26	0.41	0.02	0.001	0.02	13.3	4.33	0.97	0.051	0.029	0.0027	B:0.002	8.92
R	0.018	0.21	0.47	0.01	0.001	0.02	12.9	4.06	1.01	0.064	0.031	0.0026	W:0.24	8.74
S	0.024	0.23	0.43	0.01	0.001	0.01	12.6	4.14	0.92	0.032	0.046	0.0031	Nb:0.056, Cu:0.63, Ca:0.001, Ti:0.022	7.90
T	0.020	0.28	0.50	0.02	0.001	0.02	13.2	4.10	1.05	0.069	0.079	0.0044	Nb:0.069, Cu:0.51, Ca:0.002, B:0.001	8.49

\*) (1) 式左辺 A=Cr+Mo+0.3Si -40C -10N -Ni-0.3Mn

[0034]

[Table 2]

鋼管 No	鋼素材 No	焼入れ		焼戻し 温度 ℃	組織		引張特性		低温靱性 vE <sub>-20</sub> (J)	耐食性		備考
		温度 ℃			種類 **	残留 $\gamma$ %*	YS MPa	TS MPa		孔食の有無	腐食速度 (mm/y)	
1	A	910		560	TM + $\gamma$	2.8	948	1040	147	無	0.093	本発明例
2	B	910		550	TM + $\gamma$	2.1	960	1049	120	無	0.084	本発明例
3	C	910		550	TM + $\gamma$	3.8	920	985	127	無	0.079	本発明例
4	D	910		560	TM + $\gamma$	1.9	984	1081	196	無	0.085	本発明例
5	E	910		550	TM + $\gamma$	4.9	913	968	170	無	0.077	本発明例
6	F	910		550	TM + $\gamma$	9.7	867	971	125	無	0.074	本発明例
7	G	910		560	TM + $\gamma$	2.7	932	985	151	無	0.083	本発明例
8	H	920		540	TM + $\gamma$	1.4	974	1031	158	無	0.091	本発明例
9	I	920		540	TM + $\gamma$	5.9	911	982	109	無	0.084	本発明例
10	J	920		560	TM + $\gamma$	2.5	967	1045	195	無	0.043	本発明例
11	K	920		560	TM + $\alpha$	—	939	1170	42	有	0.079	比較例
12	L	920		560	TM + $\gamma$	10.3	933	992	76	有	0.175	比較例
13	M	920		620	TM + $\gamma$	13.2	843	983	152	無	0.096	比較例
14	N	920		560	TM + $\alpha$	—	932	987	33	有	0.084	比較例
15	O	920		620	TM + $\gamma$	12.4	838	966	163	有	0.074	比較例
16	P	920		550	TM + $\gamma$ + $\alpha$	0.5	961	1041	48	無	0.097	比較例
17	Q	920		560	TM + $\gamma$	3.1	938	1014	141	無	0.079	本発明例
18	R	920		560	TM + $\gamma$	3.6	917	986	156	無	0.081	本発明例
19	S	920		560	TM + $\gamma$	2.7	946	1012	127	無	0.097	本発明例
20	T	920		560	TM + $\gamma$	2.1	965	1068	144	無	0.085	本発明例

\* ) 面積率  
 \*\* ) TM : 焼戻しマルテンサイト  
 $\gamma$  : オーステナイト  
 $\alpha$  : フェライト

[0035] Each example of this invention has the high intensity beyond YS:860MPa, and has the low temperature toughness whose absorbed energy  $vE_{-20}$  in -20 \*\* is more than 100 J and high intensity and which was excellent, and, moreover, a corrosion rate by less than 0.1 mm/y. It is the steel pipe where generating of pitting was not seen, either but which was excellent also

in CO-proof<sub>2</sub> corrosiveness. On the other hand, in the comparative example which separates from the range of this invention, the high intensity beyond YS:860MPa was not obtained, or low temperature toughness has deteriorated, or generating of 0.1 or more mm/y and pitting was accepted, the corrosion rate lent, and CO-proof<sub>2</sub> corrosiveness has deteriorated.

[0036] Thus, this invention steel pipe is high intensity, and is excellent in low-temperature toughness and carbon dioxide-proof corrosiveness, and is understood that it is usable enough as an oil well pipe in the oil well environment of the cold district containing carbon dioxide.

[0037]

[Effect of the Invention] As mentioned above, the high intensity which can fully be used as an oil well pipe used by a harsh environment according to this invention, It is stabilized cheaply, the high strength martensitic stainless steel tube which has sufficient corrosion resistance under the hot severe corrosive environment which is high toughness and contains CO<sub>2</sub> and Cl<sup>-</sup> can be provided, and a marked effect is industrially done so.

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[Translation done.]

## \* NOTICES \*

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- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.\*\*\*\* shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

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## CLAIMS

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[Claim(s)]

[Claim 1]A high strength martensitic stainless steel tube for oil wells characterized by comprising the following which is excellent in corrosion resistance and low-temperature toughness.

At mass%, C:0.05% or less, less than Si:0.50%, Mn:0.30-1.50%, P:0.03% or less, below S:0.005 %, Cr : 11.0 to 17.0%, nickel: 7.0 [ 2.0 - ] %, below Mo:3.0 %, aluminum: A presentation which satisfies following the (1) type 0.05% or less, V:0.20% or less, and N:0.15% or less, including below O:0.005 %, and consists of the remainder Fe and inevitable impurities. An organization which contains retained austenite 10% or less.

Account Cr+Mo+0.3Si-40C-10 N-nickel-0.3Mn <=10 ..... (1)

They are Cr, Mo, Si, C, N, nickel, and the content (mass%) of Mn:each element here.

[Claim 2]A high strength martensitic stainless steel tube for oil wells which is excellent in the corrosion resistance according to claim 1 which is further characterized by containing less than Nb:0.20% at mass% in addition to said presentation, and low-temperature toughness.

[Claim 3]A high strength martensitic stainless steel tube for oil wells which is excellent in the corrosion resistance according to claim 1 or 2 which is further characterized by containing below Cu:3.5 % at mass% in addition to said presentation, and low-temperature toughness.

[Claim 4]A high strength martensitic stainless steel tube for oil wells which is excellent in the corrosion resistance according to any one of claims 1 to 3 which is further characterized by containing Ca:0.0005-0.01% at mass% in addition to said presentation, and low-temperature toughness.

[Claim 5]In addition to said presentation, at mass% further Below Ti:0.3 % and below Zr:0.2 %. A high strength martensitic stainless steel tube for oil wells which is excellent in the corrosion resistance according to any one of claims 1 to 4 containing two of one sort or the sorts or more

below W:3.0 % B:0.01% or less, and low-temperature toughness.

[Claim 6]At mass%, C:0.05% or less, less than Si:0.50%, Mn:0.30-1.50%, P:0.03% or less, below S:0.005 %, Cr : 11.0 to 17.0%, nickel: 2.0 - 7.0 %, below Mo:3.0 %, aluminum : 0.05% or less, V: Below O:0.005 % 0.20% or less and N:0.15% or less. It is tempering temperature to a this steel pipe after using as a steel pipe steel stock which has the presentation included so that following the (1) type may be satisfied by hot working. A manufacturing method of a high strength martensitic stainless steel tube for oil wells which is excellent in corrosion resistance performing temper processing made into 500 - 590 \*\*, and low-temperature toughness.

Account  $Cr+Mo+0.3Si-40C-10N-nickel-0.3Mn \leq 10$  ..... (1)

They are Cr, Mo, Si, C, N, nickel, and the content (mass%) of Mn:each element here.

[Claim 7]A manufacturing method of a high strength martensitic stainless steel tube for oil wells which is excellent in the corrosion resistance according to claim 6 performing quenching treatment cooled after heating to 890 - 950 \*\* before said temper processing, and low-temperature toughness.

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[Translation done.]